Electromechanically Active Polymer Blends for Actuation

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Actuator mechanisms that are lightweight, durable, and efficient are needed to support telerobotic requirements for future NASA missions. In this work, we present a series of electromechanically active polymer blends that can potentially be used as actuators for a variety of applications. This polymer blend combines an electrostrictive graft-elastomer with a ferroelectric poly (vinylidene fluoride-trifluoroethylene) polymer. Mechanical and piezoelectric properties of the blends as a function of temperature, frequency and relative composition of the two constituents in the blends have been studied. Electric field induced strain response of the blend films has also been studied as a function of the relative composition. A bending actuator device was developed incorporating the use of the polymer blend materials. The results and the possible effects of the combination of piezoelectricity and electrostriction in a material system are presented and discussed. This type of analysis may enable the design of blend compositions with optimal strain, mechanical, and dielectric properties for specific actuator applications.

Keywords: piezoelectric, electrostrictive, elastomer, copolymer, and actuators

1. INTRODUCTION

The ferroelectric and piezoelectric properties of poly(vinylidene fluoride-trifluoroethylene) copolymers have been extensively studied in the last two decades [1-4]. Recently, we presented a graft-elastomer polymer that exhibits a large electric field induced strain due to electrostriction [5]. This electrostrictive graft-elastomer consists of two components, a flexible backbone elastomer and grafted crystalline groups. The graft crystalline phase provides the polarizable moieties and serves as cross-linking sites for the elastomer system. In the present work, we have combined this graft-elastomer with a poly(vinylidene fluoride-trifluoroethylene) copolymer to yield several compositions of a ferroelectric-electrostrictive blend. This blend should result in an enhancement of the toughness of the copolymer since the pure copolymer is somewhat brittle. Likewise it should have a higher force output than the pure graft-elastomer when used as an actuator. Additionally, by careful selection of the composition, the potential exists to create a blend system with electromechanical properties that can be tailored for various conditions and applications.

2. EXPERIMENTAL

Film preparation: The blend films were prepared by solution casting. The ferroelectric poly(vinylidene fluoride-trifluoroethylene) copolymer (50/50 mol.%) and graft elastomer powders were added to N,N-dimethylformamide. The mixture was heated to 60°C while stirring to make a 5 wt.% polymer solution containing the desired fraction of the two components. The solution was then cooled to room temperature, cast on glass substrates, and placed in a vacuum chamber. After drying overnight under vacuum, tack-free films were obtained. In order to increase their crystallinity, and possibly their

remanent polarization, the blend films were thermally annealed at 140 °C for 10 hours. The thickness of the films was approximately 20μm.

Poling Treatment: Gold electrodes were coated on the opposing surfaces of the films using a plasma deposition method to establish electrical contact. The films were poled using a triangular waveform with a peak value of 100MV/m at 30 mHz. The blend films were immersed into silicone oil to avoid from space charge during the poling treatment.

Mechanical and Piezoelectric Measurements: The modulus, E_{11}, and the piezoelectric strain coefficient, d_{31}, of the copolymer-elastomer blend films were measured using a modified Rheovibron. These measurements were performed as a function of the relative composition of the blends (wt.% copolymer content), temperature, and frequency.

Electric Field Induced Strain Measurement: The measurement of the electric field induced strain response of the blend films in the longitudinal direction were accomplished using a fiber optic sensor (FOS) with a range of approximately 5 mils. A reflective surface was placed on one side of the electrode, while the other side was fixed to a sample holder. The FOS was positioned to measure the out-of-plane displacement through the thickness of the sample. The peak-to-peak displacement was recorded as voltage and converted into meters using the proper gains (filter gain, sensor gain and sensor sensitivity). The frequency of measurement was 1 Hz.)

3. RESULTS AND DISCUSSION

In our previous studies[6], it was observed that both the crystallinity and the remanent polarization of the copolymer-elastomer blend systems showed a linear dependence to the relative composition of the two constituents in the blends. The relationships can be expressed approximately by the equation (1) and (2), respectively.

$$X_{total} = f_{copolymer} X_{copolymer} + f_{elastomer} X_{elastomer} \qquad (1)$$

where f is the fraction of the components and X is the crystallinity. The subscripts indicate the constituents and

$$P_r = f_{copolymer} P_{r(copolymer)} + f_{elastomer} P_{r(elastomer)} \qquad (2)$$

where f is the relative fraction of the components, $P_{r(copolymer)}$ is the remanent polarization in the pure copolymer, $P_{r(elastomer)}$ is the remanent polarization in the elastomer, and $P_{r(total)}$ is the resulting remanent polarization of the blend film.

Figure 1 shows the mechanical modulus, E_{11}, for all the blends as a function of temperature at 1 Hz. As expected, the mechanical modulus of the blends increases with the increase of the copolymer content and the copolymer has the highest modulus. It is also noted that due to the brittleness of the copolymer, the pure copolymer film tended to fail at about 65 °C while the copolymer-elastomer blends show improved toughness compared to the pure copolymer.
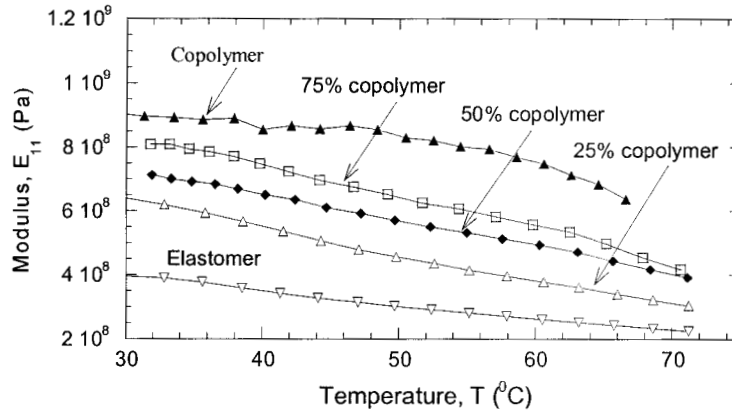
Figure 1. Comparison of the mechanical modulus E_{11} of blend films and pure polymer films.

Figure 2 shows the temperature dependence of the piezoelectric strain coefficient, d_{31}, for blend films with various compositions. The piezoelectric strain coefficient, d_{31} increases with increasing copolymer content. However, the blend film with 75 wt.% copolymer exhibits the highest d_{31} from room temperature to about 45°C. Additionally, the blend film with 50 wt.% shows an almost constant piezoelectric response from room temperature to 70°C. These results reflect the influence of both the electrical polarization and mechanical modulus of the films on the piezoelectric strain response. As observed in the case of the 75 wt.% copolymer blend, even though it had a lower remanent polarization than the pure copolymer, it showed a higher piezoelectric strain response due to its lower modulus. Improvement in the toughness of the materials is also observed. Under the present experimental conditions, the pure copolymer film breaks at a temperature close to 65°C, while the rest of the blend films maintain their piezoelectric response up to 75°C without mechanical failure. In particular, the piezoelectric strain response of the 75 wt.% copolymer and 50 wt.% copolymer blend films is still significantly high up to 75°C.

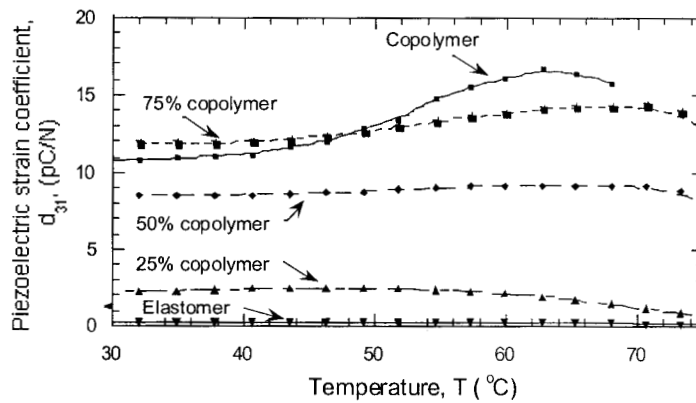
Figure 2. The temperature dependence of the piezoelectric strain coefficient, d_{31}, of the blend films (1 Hz) as a function of the various compositions.

In the blend systems, the two constituents are piezoelectric (copolymer) and electrostrictive (graft elastomer), respectively. If the two constituents make contributions, independently to each other, to the total electric field induced strain response in the blends, the total response in the longitudinal direction can be predicted by the following formula

$$S = f_{cop}.S_{cop} + f_{elast.}S_{elast.} = f_{cop}.d_{cop}E + f_{elast.}R_{elast.}E^2 \qquad (3)$$

where S is the total strain, E is the applied electric field, $f_{cop.}$ is the fraction of the piezoelectric copolymer in the blend, d_{cop} is the piezoelectric coefficient of the piezoelectric copolymer, while $f_{elast.}$ is the fraction of the electrostrictive graft elastomer, $R_{elast.}$ is the field induced strain coefficient of the electrostrictive graft elastomer. Using the reported piezoelectric coefficient of the copolymer [7] and the field induced strain coefficient of the graft elastomer calculated from electric field induced strain reported in our previous publication [6], the field induced strain in the blends is calculated. The results are shown in Figure 3a with a comparison to the strain in the pure piezoelectric copolymer and the pure
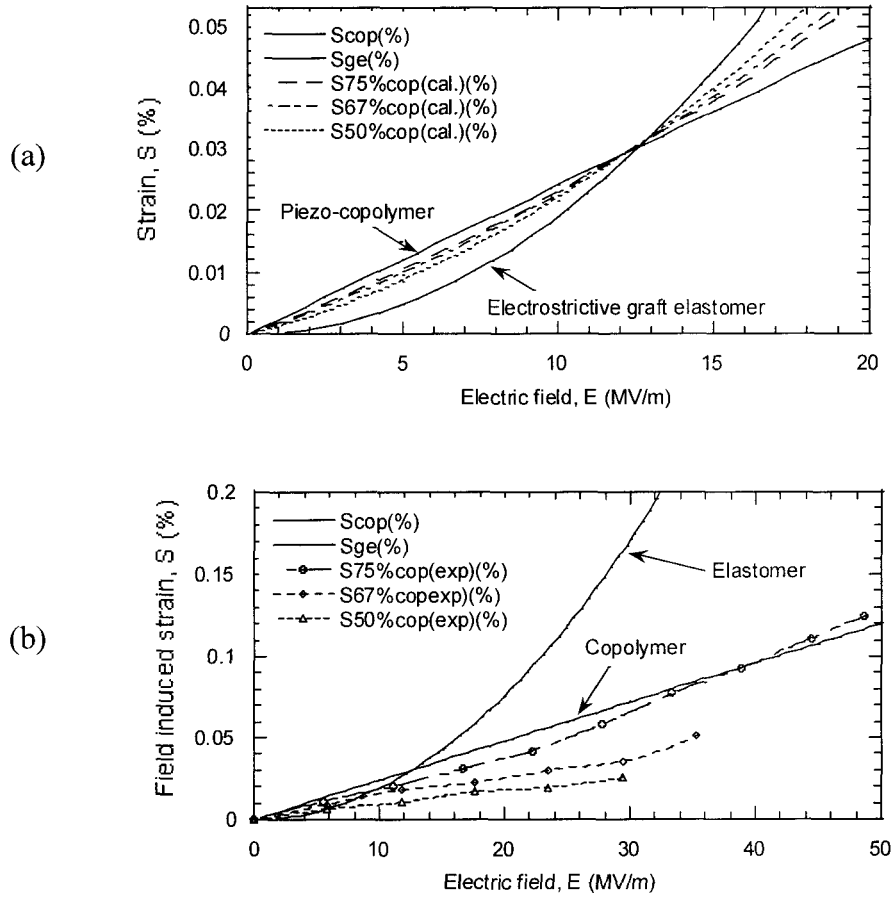
Figures 3 (a) The calculated electric field induced strain response of the piezoelectric-electrostrictive blend systems with various relative composition of the two constituents in the blends and (b) the measured electric field induced strain response of the piezoelectric-electrostrictive blends with corresponding relative composition.

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electrostrictive graft elastomer. As can be seen, the strain response of the pure copolymer is linear (piezoelectric) and the strain response of the elastomer is quadratic (electrostrictive) while the strain response of the blends is in between the strain of the two pure constituents. There is a critical electric field at about 12 MV/m. When the electric field is below the critical field, the piezoelectric constituent contributes the strain response of the blend dominantly, therefore the strain increases with the increase of the relative composition of the copolymer in the blend. When the electric field is above the critical field, the electrostrictive constituent becomes a dominant contributor to the total strain in the blends, therefore the strain response in the blend increase with the increase of the relative composition of the graft elastomer in the blend. In the Figure 3b, the experimental results of the field induced strain of the blend, in the longitudinal direction, was shown as a function of applied electric field. The relative composition of the blends used in the measurement was 50, 67 and 75 wt.% copolymer, which corresponds to the relative composition of the blends used in the prediction in Figure 3a. As can be observed, even though the strain shows obviously the dependence of the relative composition, the experimental results showed several differences when compared with the calculated prediction. (a) The measured strain response is significantly smaller than the predicted one; (b) the critical electric field for the piezoelectric dominant-electrostrictive dominant transition is obviously shifted from the prediction to a higher field; and (c) the electrostrictive contribution can not be obviously observed until the applied electric field is high enough. These differences strongly indicate that the contributions of the two constituents in the blend to the total strain response of the blend are not independent to each other. Somewhat interactions between them can affect their contributions to the strain response, especially the contribution from the electrostrictive graft elastomers.

The piezoelectric contribution to the total strain is attributed to the remanent polarization in the crystals of the copolymer in the blend, while the electrostrictive contribution to the total strain is controlled by the ability of the polar component in the elastomer to rotate following the applied electric field. Therefore, the piezoelectric contribution is expected to be proportional to the relative composition of the piezoelectric copolymer in the blend. However, the electrostrictive contribution is controlled by the environmental around the electric field rotatable polar component in the elastomer since the surroundings might change the barrier energy for the polar components to overcome and make the electric field driven rotation occur. Consequently, in the blend systems, the graft elastomer constituent may not affect the piezoelectric contribution of the copolymer very much. However, the copolymer may make the electrostrictive contribution of the elastomer more difficult since the copolymer component in the blend occupies free volume, which makes rotation of the polar component realizable in much easier way in the pure elastomer. This is very possibly the intrinsic reason for the differences observed in the experimental results from the prediction.

In Figure 4, the experimental result of 75 wt.% copolymer blend is compared with the prediction calculated using the equation (3) as a function of the applied electric field for a detailed discussion about effects of the interaction between the two constituents on the strain response in the piezoelectric-electrostrictive blend systems. For the calculated results of the strain of the 75 wt.% copolymer blend, the critical electric field for the piezoelectric dominant-electrostrictive dominant transition is 12 MV/m, (marked as 1) where the pure copolymer and the pure elastomer give equal strain response. However, for the experimental result, the strain response shows a linear increase before the electric field is raised to about 22 MV/m (marked as 2). This indicates that piezoelectric contribution to the strain is dominant. As the electric field is increased, the contribution of the electrostrictive elastomer becomes significant as

seen by the deviation from linearity above an electric field of 22 MV/m. When the electric field becomes higher than 39 MV/m, the strain of the blend becomes larger than that of the pure copolymer.
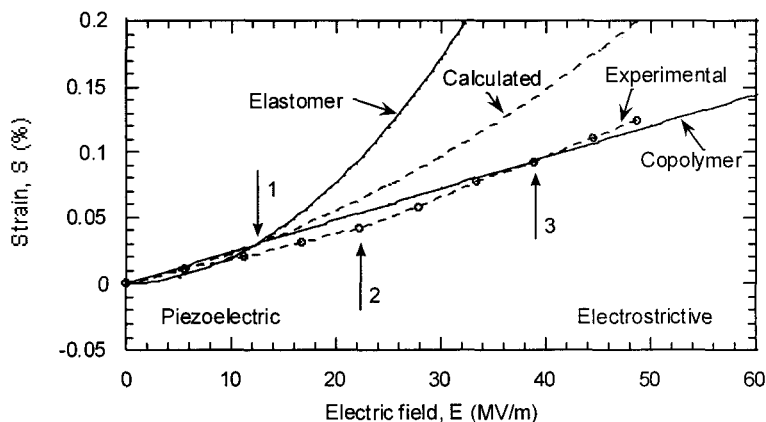

Figure 4   Comparison between the experimental strain response of the 75 wt.% copolymer blend with the prediction based on the calculation using the equation (3).

This is an indication that the electrostrictive contribution becomes dominant and the field of 39 MV/m (marked 3) is believed to be the critical electric field for the piezoelectric dominant-electrostrictive dominant transition for the 75 wt.% copolymer blend system. As can be seen, it is significantly higher than the calculated one.

According to these observations, the strain response of the blend can be divided into three regions: piezoelectric dominant region, intermediate region, and electrostrictive dominant region. In the piezoelectric dominant region (E<22 MV/m), the contribution of the electrostrictive constituent is not significant since the rotation of the polar component of the elastomer is confined due to the existence of the copolymer constituent, which increases the barrier energy for the rotation. In the intermediate region (22MV/m<E<39 MV/m), the applied electric field is increased to be high enough to overcome the increased barrier energy, therefore, the electrostrictive contribution becomes obvious indicated by the derivation of the strain from the linear trend. In the electrostrictive dominant region (E<39 MV/m), the applied electric field is high enough to overcome even higher barrier energy and promote the contribution of the electrostrictive constituent. Therefore, the electrostrictive contribution, which is quadratic to the applied electric field, becomes dominant, and the blend film shows the electric field induced strain even higher than that of the pure piezoelectric copolymer. The increase in the barrier energy for the electrostrictive contribution caused by the addition of the copolymer into the elastomer should be dependent to the relative copolymer content in the blends, morphology of the two constituents in the blend, and the distribution of the crystal size of the constituents. More extensive investigation is undergoing for further understanding.

Figure 5a illustrates the strain response of the blends with various compositions (50 wt.%, 67 wt.%, and 75 wt.%. copolymer contents) under lower electric field (E<12 MV/m). Since this is in the piezoelectric dominant region, the strain responses show basically the linear trend as a function of the applied electric field. The strain response in the blends is intermediate to the response of the pure graft-elastomer and the pure copolymer for electric field strengths less than about 5 MV/m and the strain response increases as

the piezoelectric copolymer content is increased. The direct view of the relationship between the strain response and the piezoelectric constituent content, at the electric field of 3MV/m, is shown in the figure

(a)

(b)
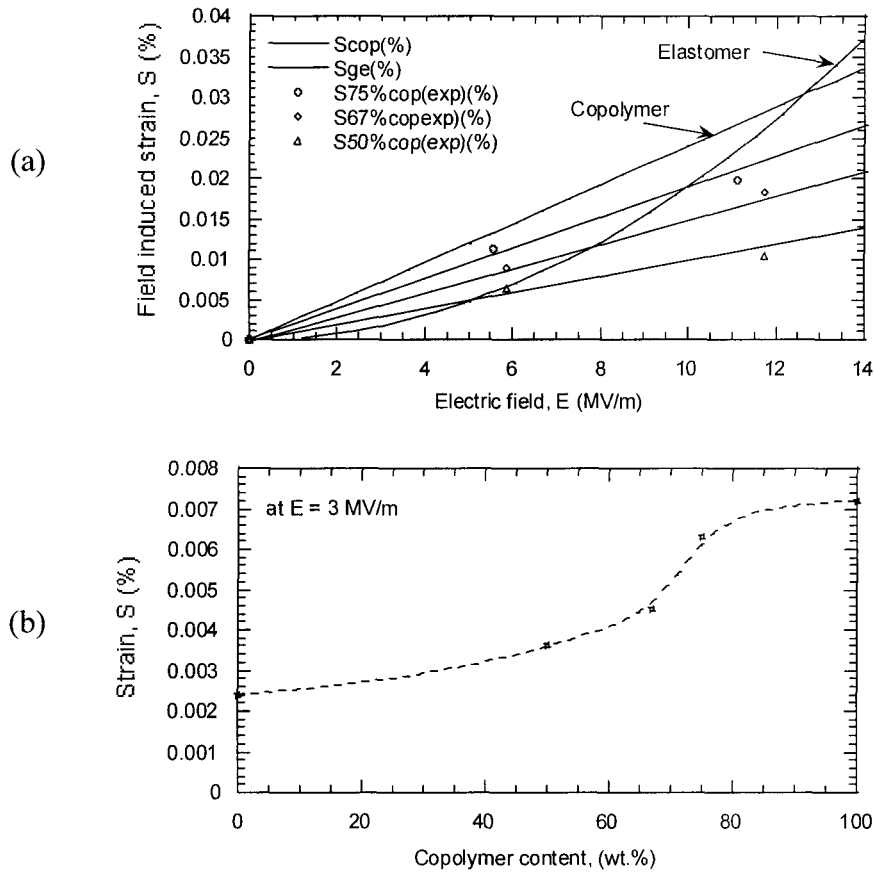
Figures 5 (a) The electric induced strain of the blends with various copolymer contents under the low electric field, and (b) the electric field induced strain of the blends as a function of the copolymer content in the blends at the electric field of 3 MV/m.

5 (b). For the 75 wt.% copolymer blend, the strain response is almost three times of that of the pure elastomer and it is only about 8% lower than that of pure copolymer. With the consideration that the improved toughness of the blend compared to the pure copolymer, and the enhanced strain response and the mechanical modulus compared to the pure elastomer, as previously discussed in mechanical and piezoelectric properties studies, it is believed that the piezoelectric-electrostrictive polymer blend systems offer a way to optimize electromechanical properties for applications at lower electric field.

Figure 9 depicts a prototype bending actuator fabricated using a film of the 50 wt.% composition of the copolymer-elastomer blend. The deflection of the bending actuator is determined by the applied electric field and the electric field induced strain of the blend. A deflection of approximately 4.5 mm was achieved with this actuator with the length of 22 mm. Larger deflections are achievable if the actuator is fabricated using the pure graft-elastomer; however, there is a trade-off between actuation force and deflection due to the relative moduli of the materials.

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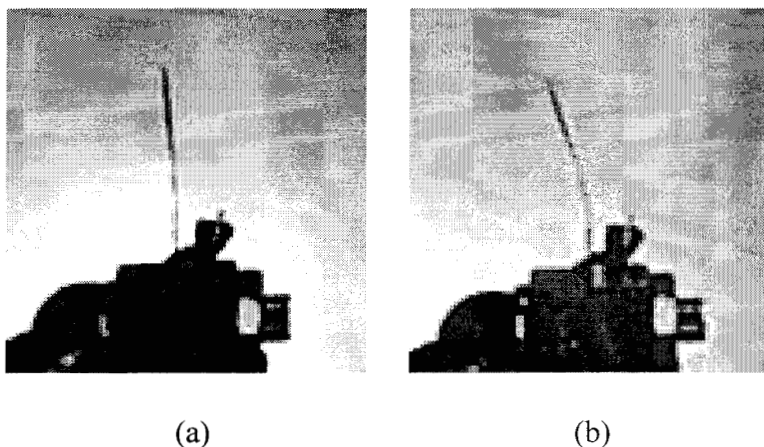<div align="center">(a)   (b)</div>

Figure 9. A bending actuator incorporating a copolymer-elastomer blend (a) no electric field is applied and (b) an electric field is of 90 MV/m is applied

4. CONCLUSION

The ferroelectric copolymer electrostrictive graft-elastomer blend system exhibited a marked improvement in toughness as compared to the pure copolymer. The blends also offer the potential of varying the composition of the material constituents to tailor the properties for desired applications. Due to the synergistic effect of the contributions of the remanent polarization and the mechanical stiffness, the blend system can be made to exhibit a higher piezoelectric strain response than the pure copolymer. As an example, the blend containing 75 wt.% copolymer exhibited a higher piezoelectric strain coefficient (d_{31}) than the pure copolymer from ambient conditions to about 45 C. Furthermore, by adjusting the relative fraction of the two components in the blend, a temperature-independent piezoelectric strain response was achieved such as in the case of the 50 wt.% copolymer. The electric field induced strain (through thickness strain) was shown to increase with increasing copolymer content. A prototype bending actuator fabricated from the 50 wt.% copolymer blend film was shown to exhibit a significant field induced deflection.

5. REFERENCES

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